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Water-Soluble Polymeric Materials with the Ability to Bind Metal Ions

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SUMMARY: Water-soluble polymers containing carboxylic acid, phosphonic acid, and sulfonic acid groups were investigated as polychelatogens by means of the liquid phase polymer-based retention technique, LPR, under different experimental conditions. The retention profiles were determined and the maximum retention capacity (MRC) of these polymers was determined at different pH and polymer-metal ion ratio. The metal ions investigated were: Ag(I), Cu(II), Co(II), Ni(II), and Cr(III). An important effect of the pH and the ligand type was observed on the metal ion retention. The MRC values of the divalent metal ions were very similar and higher than that for the trivalent cation, indicating that the polymer-metal ion interaction was basically of an electrostatic type.

Introduction

Polymeric supports with complexing groups have been widely investigated and applied for metal recovery from dilute solutions, such as industrial fluids and waste waters. Water-soluble functional polymers containing ligands at the main or side chains have been investigated for the removal of metals in the homogeneous phase.[1-6] These chelating polymers, termed *polychelatogens*, have been prepared by functionalizing various basic polymers. Water-soluble polymers are commercially available or can be synthesized by different routes. Among the most important requirements for technological applications of these polymers are their high solubility in water, an easy and cheap route of synthesis, an adequate molecular weight and molecular weight distribution, good chemical stability, high affinity for one or more metal ions, and

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selectivity for the metal ion of interest. The most usual synthetic procedures are addition polymerization, especially radical polymerization, and functionalizing of polymer backbones through polymer-analogous reactions. The macromolecules can be homo- or copolymers, and may contain one or more coordinating and/or charged groups. These groups are placed at the backbone, or at the side chain, directly or through a spacer group. Using these polychelatogens in combination with membrane filtration, higher efficiency and selectivity of membrane separations can be achieved.

This method, based on the retention of certain metal ions by a membrane which separates low molecular mass compounds from macromolecule-metal ion complexes, is called *liquid-phase polymer-based retention* (LPR). This technique uses solutions of polychelatogens in combination with membrane filtration, and selective separations of metal ions can be achieved. When solutions of mixtures of metal ions are contacted with the polymer solution, a profile for the retention of the different metal ions by the polychelatogen during the filtration can be obtained. This technique also allows the calculation of the maximum retention capacities of polymers for a metal ion. [4]

A series of polymers has been designed and investigated with respect to the analytical determination of metal ions. Poly(ethyleneimine)-based reagents have been used in many studies as complexing ligands, as well as a versatile source of chelating derivatives for removing metal ions from aqueous solutions by means of complexation-ultrafiltration (UF). [4, 5, 7-12] Among these, poly(ethyleneimine)-methyl phosphoric acid was tested as a macromolecular reagent for the isolation and analysis of plutonium in contaminated waters from the area near to the Chernobyl nuclear power plant.[10] Poly(acrylic acid) and copolymers with acrylamides[13-14], N-maleyl glycine [15], N-vinyl-2-pyrrolidone[14], poly(2-acrylamido-2-methyl-1-propane sulfonic acid)[16], poly(N-acryloyl-N-methyl piperazine)[17], as well as mixtures of two polychelatogens [18] were investigated for their ability to bind di- and trivalent cations.

LPR Technique

Hydrophilic polymers with complexing groups were tested to show the applicability of the method for the separation of various metal cations for analytical and technological purposes. The method *liquid-phase polymer based retention* (LPR) is based on the retention of certain ions by a membrane which separates low molecular mass compounds from macromolecular complexes of the ions. Thus, uncomplexed inorganic ions can be removed via the filtrate, whereas the water-soluble polymer complexes are retained (see figure 1).

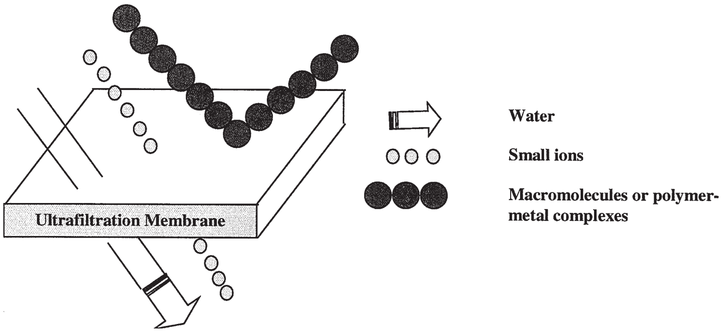


Fig. 1 Ultrafiltration Process

Different modes of separation by LPR can be used for inorganic ions. To separate the components of a small volume sample in analytical chemistry (relative preconcentration), the liquid sample is placed in the polymer containing cell solution and then washed with water (washing method). The pH is adjusted to a value at which the ions of interest are retained and the other species are removed. The washing method can also be applied to purify a macromolecular compound by eliminating the microsolutes, maintaining a constant volume in the cell.

To achieve enrichment of the metal ions, a solution can be passed from a reservoir to a smaller volume filtration unit in the presence of a complexing polymer. This concentration method (enrichment method) is designed for metal recovery from dilute technological solutions and for absolute preconcentration of elements in analytical chemistry. However, interfering components of the test solution remain partly in the cell after the filtration run, even they do not interact with the reagent. This can cause difficulties, *e.g.* in trace analysis of highly mineralized waters. To avoid this, a combined procedure is applied to both absolute and relative preconcentrations.

Figure 1 shows the principle of the procedure used for preconcentration of metal ions. The main features of a *liquid-phase polymer-based retention* system are the membrane filter, reservoir and pressure source, *e.g.* a nitrogen bottle. Conventional stirred filtration cells or a specially designed tangential-flow cell equipped with a pump can be used. Essential parameters are the molecular mass exclusion rate in a wide pH range (1-12), an appropriate permeate flow rate (0.5-12 mL min^{-1}), retentate volume (2-50 mL) and gas pressure 300 kPa. The figures given in brackets are what are suitable in most cases. A polymer concentration of 0.5-5 weight-% in the cell solution is appropriate for both retentions of elements and their subsequent determination in the retentate. The most usual molecular mass cut-off ranged between 1000 and 300000 Daltons. A nominal exclusion rate of 10 kg mol^{-1} proved to be convenient for polymers having a molecular mass ranging between 30 and 50 kg mol^{-1}.

These water-soluble polymers can be synthesized by different routes such as radical, cationic, and spontaneous polymerization, but the most usual synthetic procedures are addition polymerization, especially radical polymerization, and by functionalizing polymer backbones through polymer-analogous reactions. The polychelatogens may be homo- and copolymers, and can contain one or more ligand or coordinating groups. These groups are placed at the backbone, or at the side chain, directly or through a spacer group.

The advantages of this separation method, stems from the use of a selective binding, and the low energy requirements involved in UF.

The most common ultrafiltration membranes are based on cellulose acetate (CA), polysulfone (PS), poly(ether sulfone) (PES), polyacrylonitrile (PAN) and poly(vinyldiene fluoride) (PVDF). Although CA-based membranes are less prone to fouling and typically have a higher flux than PS membranes at equivalent rejection, PS membranes are used in many applications because of their higher stability. Moreover, hydrophobic polymers and membranes can be modified to increase flux and reduce fouling. These membrane modification techniques include the following: entrapping a hydrophilic moiety, reacting the base polymer with hydrophilic pendant groups, blending polymers, modifying the membrane surfaces, modifying the membrane charge and grafting the ceramic membranes.

Ultrafiltration membranes have larger pore sizes than reverse osmosis membranes (0.001-0.1 µm). Because of the low or negligible osmotic pressure of macrosolutes, ultrafiltration operates at very low pressures (30-80 psi).

Ultrafiltration membrane separation depends on the membrane pore size, solute-membrane interaction, and shape and size of the macromolecule. For maximum separation efficiency there should be a 10-fold difference in the sizes of the species in order to be separated. In addition, because all ultrafiltration membranes have a certain pore size distribution, the molecular mass cut off (MMCO) of the membrane (defined as the molecular weight at which 90% of the macromolecular solute is rejected by the membrane) should be at least one-half that of the smallest macromolecule that must be rejected.

The Nature of the Polymer-Metal Ion Interactions

Interactions of metal ions with water-soluble polymers are mainly due to electrostatic forces and the formation of coordinating bonds. Other weak interactions may appear as trapping metal ions in the bulk of the polymer phase.

The coordination features between polymers and metal ions may be described by the usual coordination theories, but some special aspects may be considered. When intrachain complexes are predominant, the existence of a polymer domain with near constant concentration of ligands is normally recognized, since the distances between them are kept in a narrow range for a given polymer chain. This is why the chelating reaction appears as a one-step reaction. For relatively low ligand amounts in the solution, completely complexed metal ions may coexist with free, uncomplexed ones. The reactivity of the complexes is sometimes strongly affected by the polymer ligand that exists outside the coordination sphere and surrounds the metal complex, by means of a special chemical environment and steric effects.

Electrostatic interactions between polymers and metal ions are found in many important biopolymers and synthetic polyelectrolytes. There has been a great interest in studying the interactions between polyions and the small ions (counterions) around the polyions, as this information is frequently crucial to the functioning of polyelectrolytes in technological and *in* *vivo* processes. Three different modes of counterion binding may be distinguished: territorial binding, site binding, and hydrophobic binding (adsorption). Under purely long-range electrostatic interactions, counterions tend to be nonspecifically bound to the polyion, and they are able to move along the axis of the polymer chain.

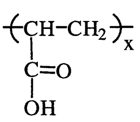
The aim of this paper is to compare the metal ion retention properties of water-soluble polymers containing carboxylic acid, sulfonic acid, and phosphonic acid directly bound to the backbone through the LPR technique under different experimental conditions.

Polychelatogens

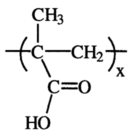
Poly(acrylic acid) (PAA), poly(methacrylic acid) (PMA) and poly(2-acrylamido-2-methyl-1-propane sulfonic acid) (PAPSA), were synthesized from the respective monomers by radical polymerization. Subsequently the polymers were purified by dissolving in water and passing through an ultrafiltration membrane with a molecular mass cut-off of 3.000 D. The final product was lyophilized.

The polyvinylphosphonic acid (PVPH), Polyscience, was further purified.

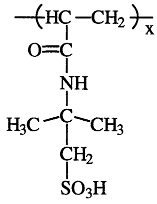
The structures of the four polychelatogens are the following:



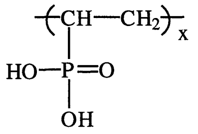
PAA



PMA



PAPSA



PVPH

Procedure to Investigate the Metal Ion Binding Properties

The membrane filtration, with Filtron, 5.000 g mol^{-1}, poly(ether sulfone)], was carried out in a system described previously. [4,11] For the determination of the complex binding ability, 0.02 M aqueous solution of the polychelatogen was prepared and adjusted to the corresponding pH by addition of diluted HNO_3 or NaOH. The solutions of polymer and metal nitrates (0.0008 M) were placed in the filtration cell. The total volume in the cell was kept constant at 20 mL. The system was pressurized by nitrogen gas and the pressure maintained at 300 kPa during the membrane filtration. The filtration fraction (Z = 1-10) was recollected and the concentration of metal ions in the filtrate was determined by atomic absorption spectrometry. *Z* is defined as the ratio of the volume in the filtrate (V_f) to the volume of the cell solution (V_o).

The maximum retention capacity (MRC) for Ag(I), Co(II), Ni(II), Cu(II), and Cr(III), was also determined. This was done by the enrichment method, according to the liquid-phase polymer based retention (LPR) technique. In this method, a metal ion solution of known concentration is passed through a solution of PAA, PMA, PAPSA, and PVPH (20 mL). The volume of the polymer solution is kept constant and the metal ion content is determined in the different filtrate volumes. With these data, the plots of metal ion concentration in the filtrate as a function of filtrate volume are obtained. For this study, 0.8 mmol of repeat units of each polychelatogen was dissolved in 20.0 mL of double-distilled water and the respective pHs adjusted. According to the solubility properties of the metal ions three pHs were studied: 3, 5, and 7. The metal ion content of the filtrates was determined by atomic absorption spectroscopy.

Polymer-Metal Ion Retention Properties

Retention versus the filtration factor, Z, can be plotted and a retention profile obtained. R is the fraction per unit of metal ions remaining in the cell. As an example, Figure 2 shows several retention profiles obtained by PMA for different metal ions.

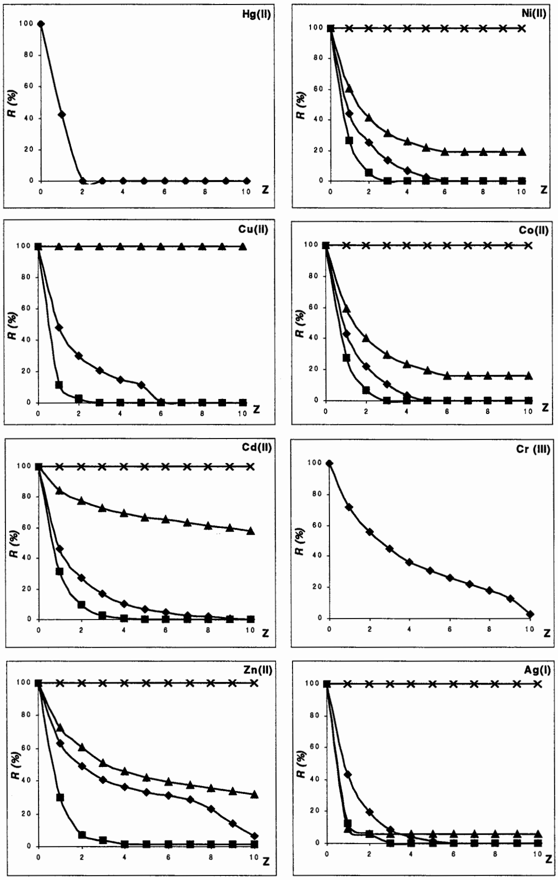


Fig. 2 Retention profiles for poly(methacrylic acid) PMA at pH (◆) 1; (■) 3; (▲) 5 and (✶) 7

The polymer-metal ion interaction is pH-dependent. In strongly acidic solutions no complexation takes place. At pH 3 no metal ion was significantly retained. At pH 5 the highest retention (100%) was obtained for Cu(II) ions. Cr $^{3+}$ ions precipitate at this pH and was not investigated. At pH 7, the Ag(I), Cd(II), Co(II), Ni(II) were retained 100%. At this pH all the carboxylic acids are dissociated and the carboxylate groups form more stable complexes with the divalent cations. Cu(II) precipitates at this pH, therefore it was not investigated.

It is well known that the filtration factor, Z, is a measurement of the strength of the ligand-metal ion interaction. At adequately high Z values a remaining residue of metal ions, which cannot be eluted by filtration at the same pH and under the same conditions, is frequently found. Therefore, Figure 3 shows that the metal ions Ag(I), Ni(II), Co(II), Cd(II), and Zn(II) form very stable complexes with carboxylate groups at pH 5 and pH 7. At pH 3 the strongest complex was formed with Cr(III). Hg(II), Cu(II), and Cr(III) were not investigated in all pH ranges (to avoid precipitation.)

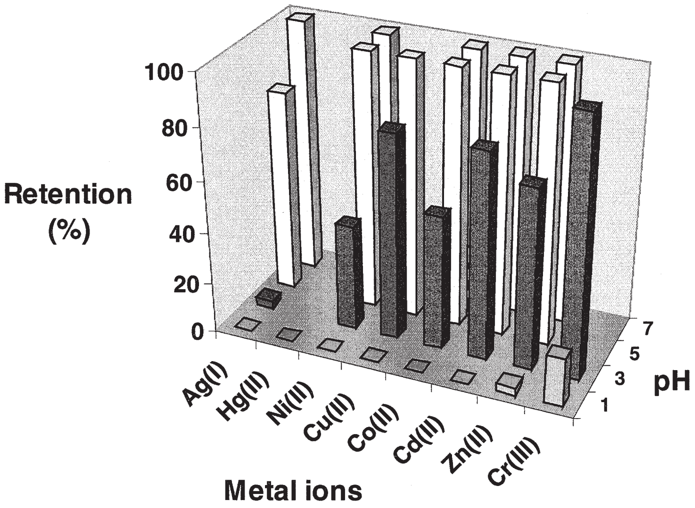


Fig. 3 Metal ion retention of PVPH at different pHs and Z=10

Figure 4 shows the metal ion binding properties of the polychelatogens containing the three ligand types. These experiments were carried out at pH = 7 corresponding to the maximum retention and Z = 10. PVPH shows a very strong affinity to form complexes with all the metal ions. Only Cu(II) is significantly retained by PVPH. The lowest affinity for the metal ions was observed for the carboxylic/carboxylate groups.

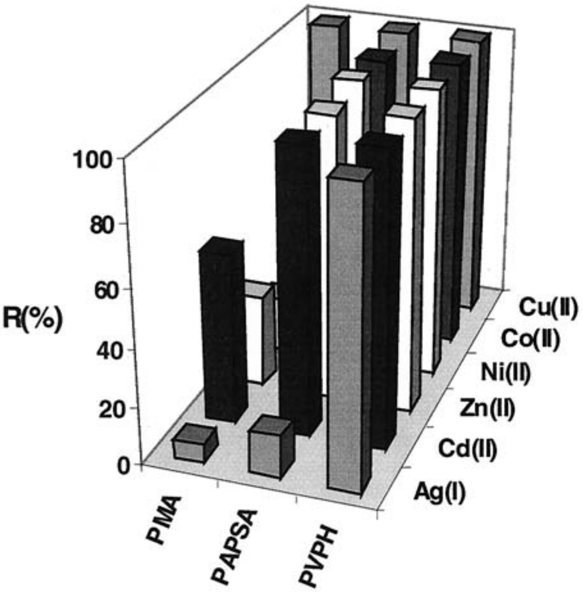


Fig. 4 Metal ion retention for the three polychelatogens at Z = 10 and pH = 7

The capacity of soluble polymer complexing agents is influenced by various factors, mainly steric and statistical ones. Usually not only intramolecular complexation takes place, but also intermolecular complexation, because the coordination number of metal ions is greater than two. The dependence of capacity on the concentration of the polymer solution differs from one polymer to another.

Generally, sterical hindrance diminishes the capacity if a certain concentration of solution is exceeded. The maximum retention capacity MRC, is defined as:

$$\mathrm{MRC} = \mathrm{M} \times \mathrm{V/Pm}$$

where, MRC = mg of metal ion retained per g of polymer M = initial concentration of metal salt (mg/L) V = metal free volume of the membrane filtrate (L) Pm = mass of polymer (g).

Table 1 MRC values for the polychelatogens at different pH values. (Metal ion concentration: 4.0 mM.)

Polychelatogen	Metal ion	Maximum Retention Capacity (MRC) (mol metal ion/mol repeat unit) pH 3	5	7
PAA	Cr^{3+}	0.0	(1)	(1)
	Cu^{2+}	0.0	(2)	(1)
	Ni^{2+}	0.0	0.0	(2)
	Co^{2+}	0.0	0.06	0.25
	Ag^{+}	0.0	0.54	0.97
PMA	Cr^{3+}	0.0	(1)	(1)
	Cu^{2+}	0.0	0.0	(1)
	Ni^{2+}	0.0	0.0	0.21
	Co^{2+}	0.02	0.07	0.25
	Ag^{+}	0.0	0.0	0.0
PAPSA	Cr^{3+}	0.14	(1)	(1)
	Cu^{2+}	0.26	0.41	(1)
	Ni^{2+}	0.32	0.42	0.43
	Co^{2+}	0.34	0.41	0.43
	Ag^{+}	0.92	1.05	1.02
PVPH	Cr^{3+}	(2)	(1)	(1)
	Cu^{2+}	0.1	0.13	(1)
	Ni^{2+}	0.0	0.0	0.0
	Co^{2+}	0.12	0.21	0.20
	Ag^{+}	0.0	0.0	0.0

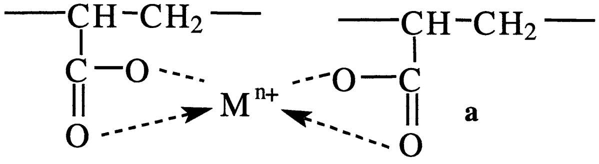
(1)At this pH the metal ion precipitates

(2)At this pH the polymer-metal ion complexe precipitates

A very strong dependence exists between capacity and pH, influenced by both the type of functional group and type of metal ion. In some cases, if the solubility of the polymer complex causes problems, it is recommendable to carry out reactions at a lower pH. Thereby, the macromolecular complex remains water-soluble. The MRC values for the four polychelatogens are summarized in Table 1. The polychelatogens PAPSA and PAA showed the highest MRC values. For Ag(I) these values are 0.97 and 1.02 mmol metal ion/mol repeat unit at pH = 7, respectively. There is a clear difference between the MRC values for the divalent and trivalent metal ions; it is lower for Cr(III). The MRC for the divalent cations are very similar. This demonstrates that the polymer-metal ion interaction is of the electrostatic type, explaining why the MRC values for a trivalent cation like Cr(III) are lower than those of the divalent cations. This is why one Cr^{3+} ion will interact with three negative charges of the repeat units of PAPSA, whereas a divalent cation such as Co^{2+} will only interact with two charges. Hence, to completely neutralize the charges in PAPSA, partially or completely dissociated, a higher number of divalent ions than of trivalent cations will be necessary, and consequently the MRC of the former will be higher.

Polymer-Metal Ion Interaction Mechanism

The polymer-metal ion interaction mechanism is strongly related to the dissociation degree of the polychelatogens. Thus, for PMA and PAA, at pH 5 most of the ligand groups are as carboxylates. Therefore, these groups form polymer-metal complexes, as shown in Figure 5a. PVPH also forms stable complexes with the metal ions (see Figure 5c). PAPSA is deprotonated at a lower pH than carboxylic acids and therefore shows a higher metal ion retention capability. For this polychelatogen, the polymer-metal ion interaction is only an electrostatic type (see Figure 5b).



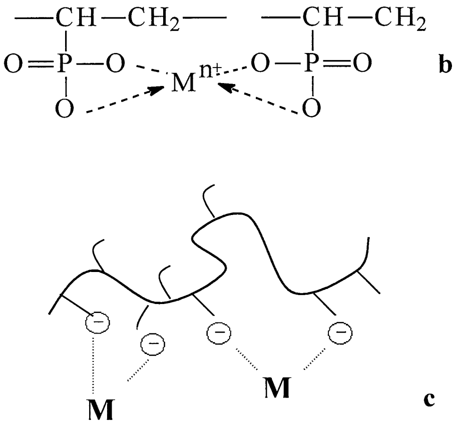


Fig. 5 Possible polymer-metal ion interaction mechanisms for a) carboxylate group (complex formation), b) phosphonate group (complex formation) and c) sulfonate group (electrostatic interaction)

Acknowledgements

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